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(54) Title: FABRIC SOFTENER COMPOSITIONS		
(57) Abstract The present invention relates to rinse-added fabric softening compositions comprising from about 5 % to about 50 % biodegradable softener active, from about 0.2 % to about 20 % silicone having a viscosity of from about 2 to about 5000 cSt, and the balance being an aqueous solvent system optionally containing low molecular weight organic solvents that are highly soluble in, or miscible with water. Fabrics treated with these compositions have superior re-wet characteristics.		

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FABRIC SOFTENER COMPOSITIONS

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TECHNICAL FIELD

10 The present invention relates to textile treatment compositions. In particular, it relates to textile softening compositions for use in the rinse cycle of a textile laundering operation to provide fabric softeners having improved biodegradability, excellent fabric
15 softening/static control benefits, and improved rewettability.

BACKGROUND OF THE INVENTION

 The art discloses problems associated with formulating fabric conditioning formulations that have
20 superior rewettability characteristics, i.e., the fabrics treated with the formulations are readily rewetted.

 Fabric softening compositions, in general, tend to diminish the ability of cotton fabrics to take up water.
25 Traditionally, there has been a trade-off between fabric softening and fabric absorbency. Normally, the use of more effective fabric softener actives and/or more fabric softener active in the rinse makes the treated fabrics, especially cotton fabrics, less water
30 absorbent. I.e., the choice has been between better softening with high performance softener compositions and better water absorbency with poor performance softener compositions.

 softener actives which maintain high fabric softening performance while having improved fabric rewettability

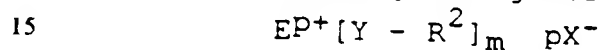
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characteristics when used after a broad range of detergent types.

SUMMARY OF THE INVENTION

The present invention relates to rinse-added fabric softening compositions comprising:

- (A) from about 5% to about 50%, preferably from about 6% to about 35%, more preferably from about 7% to about 32%, of biodegradable cationic, preferably quaternary ammonium, softener active, containing at least one, and preferably two, long hydrophobic groups, preferably with improved biodegradability as a result of the presence of ester linkages in the long hydrophobic groups, e.g., an ester quaternary ammonium softener active (EQA), preferably having the general formula:



wherein

p is 1 or 2, preferably 1;

m is 2 or 3, preferably 2;

each E is a nitrogenous quaternary group of charge $p+$;

each Y is $-O-(O)C-$, or $-C(O)-O-$;

each R^2 is a $C_{11}-C_{22}$, preferably $C_{15}-C_{17}$, hydrocarbyl or substituted hydrocarbyl substituent, preferably linear; and

each X^- is any softener-compatible anion such as chloride, bromide, methylsulfate, ethyl sulfate, formate, nitrate or the like;

- (B) from about 0.2% to about 20%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 5%, of silicone having a viscosity of from about 2 to about 5000 cSt; and

(C) the balance comprising liquid carrier selected from the group consisting of: water; low molecular weight organic solvents that are highly soluble/miscible in water such as C_1-C_4 monohydric alcohols, C_2-C_6 polyhydric alcohols, polyalkylene glycols; and mixtures thereof.

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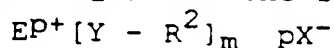
All percentages, ratios and proportions are by weight, unless otherwise specified. All numbers are approximations unless otherwise stated.

DETAILED DESCRIPTION OF THE INVENTION

5 The present invention relates to rinse-added fabric softener compositions comprising, as essential components, from about 5% to about 50%, preferably from about 6% to about 35%, more preferably from about 7% to about 32%, by weight of the composition, of
10 biodegradable cationic softener active, preferably an ester quaternary ammonium softener active (EQA) and from about 0.2% to about 20%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 5%, silicone, as described hereinafter.

15 (A) Biodegradable Cationic Fabric Softener Active

The preferred biodegradable cationic softener active containing ester linkages in the long hydrophobic groups (EQA) has the formula:



20 wherein

p is 1 to 2;

m is 2 or 3;

each E is a nitrogenous quaternary group of charge p+;

each Y is -O-(O)C-, or -C(O)-O-;

25 R^2 is the same or different C_{11} - C_{22} hydrocarbyl or substituted hydrocarbyl substituent; and

X^- is any softener-compatible anion such as chloride, bromide, methylsulfate, ethyl sulfate, formate, nitrate and the like;

30 preferably E is selected from the group consisting of:

(1) $(R)_{4-m} N^+ [(CH_2)_n]_m$ with m being 2 or 3;

(2) $(R)_3 N^+ (CH_2)_n CH - CH_2$; and

(3) mixtures thereof;

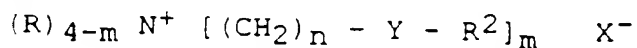
wherein

(e.g., hydroxy alkyl, preferably C_1 - C_3 alkyl group,

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e.g., methyl (most preferred), ethyl, propyl, and the like, a benzyl group, hydrogen, and mixtures thereof; wherein R_2 is derived from C_{11} - C_{22} fatty acyl groups.

A preferred EQA, with E of the formula (1) above, has the formula:



wherein: each Y = -O-(O)C-, or -C(O)-O-; m = 2 or 3; each n = 1 to 4; each R substituent is a short chain C_1 - C_6 alkyl or substituted alkyl group (e.g., hydroxyalkyl, preferably hydroxy ethyl, preferably C_1 - C_3 , alkyl, e.g., methyl (most preferred), ethyl, propyl, and the like, or substituted alkyl group (e.g., hydroxy alkyl, preferably hydroxyethyl), benzyl, or mixtures thereof, preferably alkyl; each R^2 is a long chain, preferably at least partially unsaturated, e.g., Iodine Value (IV) of greater than about 5 to less than about 100, C_{11} - C_{22} hydrocarbyl, or substituted hydrocarbyl group; and the counterion, X^- , can be any softener-compatible anion, for example, chloride, bromide, methylsulfate, formate, sulfate, nitrate and the like.

Non-limiting examples of biodegradable softener actives with E (1) are N,N-di(tallowoyloxyethyl)-N,N-dimethylammonium chloride and N,N-di(tallowoyloxyethyl)-N-(2-hydroxyethyl)-N-methylammonium methyl sulfate.

A non-limiting example of a biodegradable softener active with E (2) is 1,2-ditallowoyloxy-3-trimethylammoniopropane chloride.

EQA compounds prepared with fully saturated alkyl groups (R^2) are rapidly biodegradable and excellent softeners. However, compounds prepared with at least partially unsaturated alkyl groups have many advantages (i.e., improved concentratability and good storage viscosity stability) and are highly acceptable for consumer products. EQA with unsaturated alkyl groups provide improved fabrics with improved water absorbency as compared to EQA with saturated alkyl groups.

Variables that must be adjusted to obtain the benefits of using unsaturated acyl groups include the

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Iodine Value (IV) of the fatty acids; the cis/trans isomer weight ratios in the fatty acyl groups; and the odor of fatty acid and/or the EQA. Any reference to IV values hereinafter refers to IV of fatty acyl/alkyl groups and not to the resulting EQA compound.

When the IV of the fatty acyl groups is above about 20, the EQA provides excellent antistatic effect. Antistatic effects are especially important where the fabrics are dried in a tumble dryer, and/or where synthetic materials which generate static are used. Maximum static control occurs with an IV of greater than about 20, preferably greater than about 40. When fully saturated EQA compositions are used, poor static control results. Also, formulas with higher softener concentrations will typically require higher Iodine Values. The benefits of concentratability include: use of less packaging material; use of less organic solvents, especially volatile organic solvents; use of less concentration aids which may add nothing to performance; etc.

As the IV is raised, there is a potential for odor problems. Some highly desirable, readily available sources of fatty acids such as tallow, possess odors that remain with the compound EQA despite the chemical and mechanical processing steps which convert the raw tallow to finished EQA. Such sources must be deodorized, e.g., by absorption, distillation (including stripping such as steam stripping), etc., as is well known in the art. In addition, care must be taken to minimize contact of the resulting fatty acyl groups to oxygen and/or bacteria by adding antioxidants, antibacterial agents, etc. The additional expense and effort associated with the unsaturated fatty acyl groups

fatty acyl groups can be concentrated above about 10% without the need for additional concentration aids, especially surfactant concentration aids.

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- EQA derived from highly unsaturated fatty acyl groups, i.e., fatty acyl groups having a total unsaturation above about 65% by weight, do not provide any additional improvement in antistatic effectiveness.
- 5 They may, however, be able to provide other benefits such as improved water absorbency of the fabrics. In general, an IV range of from about 40 to about 65 is preferred for concentratability, maximization of fatty acyl sources, excellent softness, static control, etc.
- 10 Highly concentrated aqueous dispersions of diester compounds can gel and/or thicken during low (about 5°C) temperature storage. Diester compounds made from only unsaturated fatty acids minimize this problem but additionally are more likely to cause malodor formation.
- 15 Compositions containing diester compounds made from fatty acids having an IV of from about 5 to about 25, preferably from about 10 to about 25, more preferably from about 15 to about 20, and a cis/trans isomer weight ratio greater than about 30/70, preferably greater than
- 20 about 50/50, more preferably greater than about 70/30, are storage stable at low temperature with minimal odor formation. These cis/trans isomer weight ratios provide optimal concentratability at these IV ranges. In the IV range above about 25, the ratio of cis to trans isomers
- 25 is less important unless higher concentrations are needed. For any IV, the concentration that will be stable in an aqueous composition will depend on the criteria for stability (e.g., stable down to about 5°C; stable down to 0°C; doesn't gel; gels but recovers on
- 30 heating, etc.) and the other ingredients present, but the maximum concentration that is stable can be raised by adding concentration aids to achieve the desired stability.
- Generally, hydrogenation of fatty acids to reduce
- 35 polyunsaturation and to lower IV to insure good color and improve odor and odor stability leads to a high degree of trans configuration in the molecule. Therefore, diester compounds derived from fatty acyl

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groups having low IV values can be made by mixing fully hydrogenated fatty acid with touch hydrogenated fatty acid at a ratio which provides an IV of from about 5 to about 25. The polyunsaturation content of the touch hardened fatty acid should be less than about 5%, preferably less than about 1%. During touch hardening the cis/trans isomer weight ratios are controlled by methods known in the art such as by optimal mixing, using specific catalysts, providing high H₂ availability, etc. Touch hardened fatty acid with high cis/trans isomer weight ratios is available commercially (i.e., Radiacid 406 from FINA).

It will be understood that R² can optionally be substituted with various groups such as alkoxyl or hydroxyl groups. Some of the preferred compounds can be considered to be diester variations of ditallow dimethyl ammonium chloride (DTDMAC), which is a widely used fabric softener. Preferably, at least about 80% of the EQA is the diester. Preferably, less than about 20%, more preferably less than about 10%, should be EQA monoester (e.g., only one -Y-R² group).

As used herein, when the diester is specified, it will include the monoester that is normally present. The level of monoester can be controlled during the manufacture of the EQA. Preferably, some of the monoester is present. The overall ratios of diester to monoester are from about 100:1 to about 2:1, preferably from about 50:1 to about 5:1, more preferably from about 13:1 to about 8:1. Under high anionic detergent carry-over conditions, the di/monoester ratio is preferably about 11:1.

(B) Silicones

The silicone herein is either a polydimethyl siloxane (polydimethyl silicone or PDMS) or a

silicone having a molecular weight, e.g., one having a viscosity of from about 2 to about 5000 cSt, preferably from about 5 to

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about 500 cSt, more preferably from about 25 to about 200- cSt. Silicone emulsions can conveniently be used to prepare the compositions of the present invention. However, preferably, the silicone is one that is, at
5 least initially, not emulsified. I.e., the silicone should be emulsified in the composition itself. In the process of preparing the compositions, the silicone is preferably added to the "water seat", which comprises the water and, optionally, any other ingredients that
10 normally stay in the aqueous phase.

Low molecular weight PDMS is preferred for use in the fabric softener compositions of this invention. The low molecular weight PDMS is easier to formulate without preemulsification.

15 Silicone derivatives such as amino-functional silicones, quaternized silicones, and silicone derivatives containing Si-OH, Si-H, and/or Si-Cl bonds, can be used. However, these silicone derivatives are normally more substantive to fabrics and can build up on
20 fabrics after repeated treatments to actually cause a reduction in fabric absorbency.

When added to water, the fabric softener composition deposits the biodegradable cationic fabric softening active on the fabric surface to provide fabric
25 softening effects. However, in a typical laundry process, using an automatic washer, cotton fabric water absorbency is appreciably reduced when there is more than about 40 ppm, especially when there is more than about 50 ppm, of the biodegradable cationic fabric
30 softening active in the rinse water. The silicone improves the fabric water absorbency, especially for freshly treated fabrics, when used with this level of fabric softener without adversely affecting the fabric softening performance. The mechanism by which this
35 improvement in water absorbency occurs is not understood, since the silicones are inherently hydrophobic. It is very surprising that there is any

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improvement in water absorbency, rather than additional loss of water absorbency.

The amount of PDMS needed to provide a noticeable improvement in water absorbency is dependent on the initial rewettability performance, which, in turn, is dependent on the detergent type used in the wash. Effective amounts range from about 2 ppm to about 50 ppm in the rinse water, preferably from about 5 to about 20 ppm. The PDMS to softener active ratio is from about 2:100 to about 50:100, preferably from about 3:100 to about 35:100, more preferably from about 4:100 to about 25:100. As stated hereinbefore, this typically requires from about 0.2% to about 20%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 5% silicone.

The PDMS also improves the ease of ironing in addition to improving the rewettability characteristics of the fabrics. When the fabric care composition contains an optional soil release polymer, the amount of PDMS deposited on cotton fabrics increases and PDMS improves soil release benefits on polyester fabrics. Also, the PDMS improves the rinsing characteristics of the fabric care compositions by reducing the tendency of the compositions to foam during the rinse. Surprisingly, there is little, if any, reduction in the softening characteristics of the fabric care compositions as a result of the presence of the relatively large amounts of PDMS.

(C) Liquid Carrier

The liquid carrier in the compositions of the present invention is preferably water, the carrier also can optionally comprise low molecular weight organic solvent that is highly soluble in water, e.g., C₁-C₄

alcohols, and esters thereof. The water can be distilled, deionized, or tap water. Mixtures of water and up to about 15% of a short chain alcohol such as

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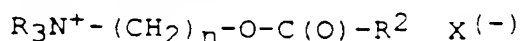
ethanol, propanol, isopropanol, and mixtures thereof are preferred carriers. Examples of these water soluble solvents include: ethanol, propanol, isopropanol, n-butyl alcohol, t-butyl alcohol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerol, propylene carbonate, and mixtures thereof.

(D) Optional Ingredients

The present invention can include other optional components conventionally used in textile treatment compositions, for example, colorants, perfumes, preservatives, optical brighteners, opacifiers, fabric conditioning agents, surfactants, stabilizers such as guar gum, anti-shrinkage agents, anti-wrinkle agents, fabric crisping agents, anti-spotting agents, germicides, fungicides, anti-corrosion agents, anti-foam agents, and the like. Especially preferred optional ingredients include dispersibility aids, stabilizers, soil release agents, and bacteriocides.

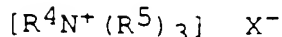
The optional dispersibility aids facilitate dispersion of the compositions of the present invention in the rinse water. They are selected from the group consisting of mono-alkyl cationic quaternary ammonium compounds, mono-alkyl amine oxides, and mixtures thereof, at a total level of from 0% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 5% by weight of the composition. These materials can either be added as part of the active softener raw material, (A), or added as a separate component. The total level of dispersibility aid includes any amount that may be present as part of component (A).

Dispersibility aids include mono-alkyl cationic quaternary ammonium compound, preferably, the monoester derivatives of the biodegradable diester fabric softener actives having the formula:



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wherein R, R², n, and X⁽⁻⁾ have the meanings as defined hereinbefore for (A); and quaternary ammonium salts of the general formula:



5 wherein R⁴ is C₈-C₂₂ alkyl or alkenyl group, preferably C₁₀-C₁₈ alkyl or alkenyl group; more preferably C₁₀-C₁₄ or C₁₆-C₁₈ alkyl or alkenyl group;

each R⁵ is a C₁-C₆ alkyl or substituted alkyl group (e.g., hydroxy alkyl), preferably C₁-C₃ alkyl group,
 10 e.g., methyl (most preferred), ethyl, propyl, and the like, a benzyl group, hydrogen, a polyethoxylated chain with from about 2 to about 20 oxyethylene units, preferably from about 2.5 to about 13 oxyethylene units, more preferably from about 3 to about 10 oxyethylene
 15 units, and mixtures thereof; and
 X⁻ is as defined hereinbefore for (A).

An especially preferred dispersibility aid is monolauryl trimethyl ammonium chloride and monotallow trimethyl ammonium chloride available from Witco under
 20 the trade name Varisoft® 471.

The R⁴ group can also be attached to the cationic nitrogen atom through a group containing one, or more, ester, amide, ether, amine, etc., linking groups which can be desirable for increased concentratability of
 25 component (A), biodegradability, etc. Such linking groups are preferably within from about one to about three carbon atoms of the nitrogen atom.

Mono-alkyl cationic quaternary ammonium compounds also include C₈-C₂₂ alkyl choline esters, preferably
 30 C₁₂-C₁₄ choline ester and/or C₁₆-C₁₈ tallow choline ester, and/or biodegradable single-long-chain alkyl dispersibility aids containing an ester linkage in the long chains as described in U.S. Pat. No. 4,840,738, Weiden and Waller, issued June 22, 1989.

When the dispersibility aid comprises a small amount of esters, preferably the compositions also contain a small amount, preferably from about 2% to about 5% by weight

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of the composition, of organic acid. Organic acids are described in EPA 404,471, Machin et al., published on Dec. 27, 1990, which is herein incorporated by reference. Preferably the organic acid is selected from the group consisting of glycolic acid, acetic acid, citric acid, and mixtures thereof.

Ethoxylated quaternary ammonium compounds which can serve as the dispersibility aid include ethylbis(polyethoxy ethanol)alkylammonium ethylsulfate with 17 moles of ethylene oxide, available under the trade name Variquat® 66 from Witco/Sherex Chemical Company; polyethylene glycol (15) oleammonium chloride, available under the trade name Ethoquad® 0/25 from Akzo; and polyethylene glycol (15) cocomonium chloride, available under the trade name Ethoquad® C/25 from Akzo.

Also, quaternary compounds having only a single long alkyl chain, can protect the diester softener from interacting with anionic surfactants and/or detergent builders that are carried over into the rinse from the wash solution.

Other suitable dispersibility aids include amine oxides with one alkyl or hydroxyalkyl moiety of about 6 to about 22 carbon atoms, preferably from about 10 to about 18 carbon atoms, more preferably from about 8 to about 14 carbon atoms, and two alkyl moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups with about 1 to about 3 carbon atoms. Examples include dimethyloctylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyl-tetradecylamine oxide, methylethylhexadecylamine oxide, dimethyl-2-hydroxyoctadecylamine oxide, and coconut fatty alkyl dimethylamine oxide.

Stabilizers can also be present in the compositions of the present invention. The term "stabilizer," as used herein, includes antioxidants and reductive agents. These agents are present at a level of from 0% to about 2%, preferably from about 0.01% to about 0.2%, more

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preferably from about 0.035% to about 0.1% for antioxidants, and more preferably from about 0.01% to about 0.2% for reductive agents. These assure good odor stability under long term storage conditions.

- 5 Antioxidants and reductive agent stabilizers are especially critical for unscented or low scent products (no or low perfume).

Examples of antioxidants that can be added to the compositions of this invention include a mixture of
10 ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG and Tenox® S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), propyl gallate, and citric acid,
15 available from Eastman Chemical Products, Inc., under the trade name Tenox®-6; butylated hydroxytoluene, available from UOP Process Division under the trade name Sustane® BHT; tertiary butylhydroquinone, Eastman Chemical Products, Inc., as Tenox® TBHQ; natural
20 tocopherols, Eastman Chemical Products, Inc., as Tenox® GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA; long chain esters (C₈-C₂₂) of gallic acid, e.g., dodecyl gallate; Irganox® 1010; Irganox® 1035; Irganox® B 1171; Irganox® 1425;
25 Irganox® 3114; Irganox® 3125; and mixtures thereof; preferably Irganox® 3125, Irganox® 1425, Irganox® 3114, and mixtures thereof; more preferably Irganox® 3125 alone or mixed with citric acid and/or other chelators such as isopropyl citrate, Dequest® 2010, available from
30 Monsanto with a chemical name of 1-hydroxyethylidene-1, 1-diphosphonic acid (etidronic acid), and Tiron®, available from Kodak with a chemical name of 4,5-dihydroxy-m-benzene-sulfonic acid/sodium salt, and DTPA®, available from Aldrich with a chemical name of

above stabilizers which can be used in the compositions of the present invention are listed in Table I below.

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TABLE I

	<u>Antioxidant</u>	<u>CAS No.</u>	<u>Chemical Name used in Code of Federal Regulations</u>
5	Irganox® 1010	6683-19-8	Tetrakis methylene(3,5-di- tert-butyl-4- hydroccinnamate)] methane
	Irganox® 1035	41484-35-9	Thiodiethylene bis(3,5-di- tert-butyl-4-hydroxyhydro- cinnamate
10	Irganox® 1098	23128-74-7	N,N'-Hexamethylene bis(3,5-di-tert-butyl-4- hydroxyhydro-cinnammamide
	Irganox® B	31570-04-4	1:1 Blend of Irganox® 11711098 23128-74-7 and Irgafos® 168
15	Irganox® 1425	65140-91-2	Calcium is[monoethyl(3,5- di-tert-butyl-4 hydroxybenzyl)- phosphonate]
20	Irganox® 3114	27676-62-6	1,3,5-Tris(3,5-di-tert- butyl-4-hydroxybenzyl)-s- triazine- 2,4,6-(1H, 3H,5H) trione
25	Irganox® 3125	34137-09-2	3,5-Di-tert-butyl-4- hydroxy-hydrocinnamic acid triester with 1,3,5-ris (2-hydroxy-ethyl)-S- triazine-2,4,6-(1H,3H, 5H)- trione
30	Irgafos® 168	31570-04-4	Tris(2,4-di-tert-butyl- phenyl)phosphite

Optionally, the compositions herein contain from 0%
to about 10%, preferably from about 0.1% to about 5%,
35 more preferably from about 0.1% to about 2%, of a soil
release agent. Preferably, such a soil release agent is
a polymer. Polymeric soil release agents useful in the
present invention include copolymeric blocks of

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terephthalate and polyethylene oxide or polypropylene oxide, and the like. U.S. Pat. No. 4,956,447, Gosselink/Hardy/Trinh, issued Sept. 11, 1990, discloses specific preferred soil release agents comprising cationic functionalities, said patent being incorporated
5 herein by reference.

More complete disclosure of highly preferred soil release agents is contained in European Pat. Application 185,427, Gosselink, published June 25, 1986, and U.S.
10 Pat. No. 5,207,933, Trinh et al., issued May 4, 1993, both of which are incorporated herein by reference.

Examples of bacteriocides that can be used in the compositions of this invention are parabens, especially methyl, glutaraldehyde, formaldehyde, 2-bromo-2-nitropropane-1,3-diol sold by Inolex Chemicals under the
15 trade name Bronopol®, and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one sold by Rohm and Haas Company under the trade name Kathon® CG/ICP. Typical levels of
20 bacteriocides used in the present compositions are from about 1 ppm to about 2,000 ppm by weight of the composition, depending on the type of bacteriocide selected. Methyl paraben is especially effective for preventing mold growth in aqueous fabric softening
25 compositions with under 10% by weight of the ester compound.

Method of Softening

In the method aspect of this invention, fabrics or
30 fibers are contacted with an effective amount, generally from about 10 ml to about 150 ml (per 3.5 kg of fiber or fabric being treated) of the softener composition (including ester, quaternary ammonium compound, and

an anionic surfactant) to soften the fabric.

depending on concentration of the composition, fiber or fabric type, and degree of softness desired. Preferably, the rinse bath contains from about 10

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about 1,000 ppm, preferably from about 50 to about 500 ppm, more preferably from about 50 to about 150 ppm, of total active fabric softening compounds herein and from about 2 ppm to about 50 ppm, preferably from about 3 ppm to about 30 ppm, more preferably from about 5 ppm to about 20 ppm silicone.

The following are examples of the present invention which are not intended to limit the present invention.

10 EXAMPLES

<u>Components</u>	I	II
	<u>Wt.%</u>	<u>Wt.%</u>
Ester Quat Compound (1)	10.1	10.1
PDMS (DC-200; 50 cSt)	1.2	--
15 PDMS (DC-200; 350 cSt)	--	1.0
HCl (25%)	0.06	0.06
CaCl ₂ (25%)	0.06	0.06
Deionized Water	Balance	Balance

20 (1) Di(soft tallowoyloxyethyl) dimethyl ammonium chloride where the fatty acyl groups are derived from fatty acids with IV of about 55, % unsaturation of about 53.1, and C₁₈ cis/trans isomer ratio of about 8.2 (% cis isomer about 40.0 and % trans isomer about 4.9); the diester includes monoester at a weight ratio of about 11:1 diester to monoester; 86% solids in ethanol.

Example I - Process

About 0.6 g of a HCl solution (25%) is added to about 886 g deionized water pre-heated to about 66°C in a stainless steel mixing tank. The water seat is mixed with an IKA mixer (Model RW 20 DZM) at about 1500 rpm using an impeller with about 5.1 cm diameter blades. About 12 g of an unemulsified Dow-Corning DC-200 50 cSt PDMS is added to the mix tank, with mixing. About 101 g of an ester quaternary ammonium compound, containing about 86% di(soft tallowoyloxyethyl) dimethyl ammonium chloride in ethanol, pre-heated to about 66°C, is then slowly added to the water seat. About 0.6 g of a 25%

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CaCl₂ solution is added and the mixture is milled, using an IKA Ultra Turrax T-50 high shear mixer (at about 10,000 rpm), for about 5 min.

Example II - Process

- 5 The making procedure of Example II is similar to that of Example I, except that about 10 g of an unemulsified 350 cSt PDMS is used instead of the 50 cSt PDMS.

<u>EXAMPLES</u>		III	IV	V
10	<u>Component</u>	<u>Wt.%</u>	<u>Wt.%</u>	<u>Wt.%</u>
	Diester Compound(1)	30.6	30.6	30.6
	Silicone			
	(DC-200®; 50cSt)	3.00	3.00	-
	Emulsified PDMS(2)	-	-	2.8
15	Hydrochloric Acid	0.018	0.0082	0.018
	Citric Acid	-	0.005	-
	Liquitint® Blue			
	651 Dye (1%)	0.27	0.27	0.27
	Perfume	1.35	1.35	1.35
20	Tenox® 6	0.035	-	0.035
	Irganox® 3125	-	0.035	-
	Kathon® (1.5%)	0.02	0.02	0.02
	DC-2210 Antifoam			
	(10%)	0.15	0.15	0.15
25	CaCl ₂ Solution			
	(15%)	4.33	3.33	4.33
	Deionized Water	Balance	Balance	Balance
	pH = 2.8 - 3.5			
	Viscosity = 35-60 cps.			

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(1) Di(soft tallowoxyloxyethyl)dimethyl ammonium chloride of Example I.

(2) Polydimethylsiloxane (PDMS) of Example I.

following process:

1. Separately, heat the diester compound premix with the Tenox 6 or Irganox 3125 and the water.

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containing HCl, citric acid (if used), and antifoam agent to 74°C (Note: for Composition IV the citric acid can totally replace HCl, if desired);

2. Add the DC-200 silicone to the water seat.
- 5 3. Add the diester compound premix into the water seat over about 5-6 minutes. During the injection, both mix (about 600-1,000 rpm) and mill (about 8,000 rpm with an IKA Ultra Turrax T-50 Mill) the batch.
4. Add about 500 ppm of CaCl_2 at approximately halfway through the injection.
- 10 5. Add 2,000 ppm CaCl_2 over about 2-7 minutes (about 200-2,500 ppm/minute) with mixing at about 800-1,000 rpm after premix injection is complete at about 65°-74°C.
6. Add perfume over 30 seconds at about 63°-68°C.
- 15 7. Add dye and Kathon and mix for about 30-60 seconds. Cool batch to about 21-27°C.
8. Add 2,500 ppm to 4,000 ppm CaCl_2 to the cooled batch and mix.

While the silicone can be added at any point in the process while the product is hot, for better stability of the viscosity over time, it is preferred to add the silicone in the water seat (as described above), or alternatively, immediately before perfume addition at about 63-68°C. In a more preferred process, the silicone is added to the water seat and mixed by milling for about 5 minutes and then about 5-10% of the diester compound premix is injected into the water seat, followed by additional milling for about 5 minutes. Then, steps 3-8 above are followed. In this process, the silicone is "pre-emulsified" to retard any silicone phase separation on long term storage.

The above Example V is prepared by a procedure similar to that of Example III, except that a Dow-Corning CF-1469 silicone emulsion, containing about 55% of a 350 cSt PDMS is used instead of the unemulsified PDMS and the emulsion is added last to the already cooled mixture.

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<u>EXAMPLES</u>		VI	VII	VIII	IX
<u>Components</u>		<u>Wt. %</u>	<u>Wt. %</u>	<u>Wt. %</u>	<u>Wt. %</u>
Hydroxyethyl					
Ester Quat (1)		9.80	9.80	--	--
5	Propane Ester				
Quat (2)		--	--	8.67	8.67
Ethanol		--	--	1.20	1.20
Emulsified PDMS (3)		2.18	--	2.18	--
PDMS (4)		--	1.20	--	1.20
10	HCl (25%)	0.05	0.05	0.06	0.06
Perfume		0.45	0.45	--	--
Dye Solution (1%)		0.08	0.08	--	--
Kathon (1.50%)		0.02	0.02	0.02	0.02
CaCl ₂ (25%)		0.06	0.06	0.06	0.06
15	Deionized Water	Balance	Balance	Balance	Balance

(1) Di(tallowoyloxyethyl)(2-hydroxyethyl)methyl ammonium methyl sulfate, 85% active in ethanol.

(2) 1,2-di(hardenedtallowoyloxy)-3-trimethylammoniopropane chloride.

(3) Dow-Corning CF-1469 emulsified 350 cSt PDMS (55% PDMS)

(4) Dow-Corning DC-200 50 cSt PDMS.

Processes for making EXAMPLES VI -IX.

25 Example VI

About 0.5 g of a HCl solution (25%) is added to about 874 g deionized water pre-heated to about 70°C in a 1.5L stainless steel mix tank. This "water seat" is mixed with an IKA mixer (Model RW 25) at about 1000 rpm using an impeller with about 5.1 cm diameter blades. About 21.8 g of a Dow-Corning CF-1469 silicone emulsion, containing about 12 g of a 350 cSt PDMS, is added to the mix tank, with mixing. About 98 g of Stepanquat 6585-ET

water seat, by injection at the impeller blades via a peristaltic pump. The mixture is cooled during mixing, and about 4.5 g of perfume, about 0.2 g of a 1.5% Kathon

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solution, and about 0.8% of a 1% dye solution are added when the mixture temperature reaches about 45°C. About 0.6 g of a 25% CaCl_2 solution is added when the mixture temperature reaches about 27°C. The mixing is stopped when the batch temperature reaches about 24°C.

Example VII

The making procedure of Composition VII is similar to that of Example VI, except that about 12 g of an unemulsified 50 cSt PDMS is used instead of the 350 cSt PDMS emulsion.

Example VIII

About 0.6 g of a HCl solution (25%) is added to about 878 g deionized water pre-heated to about 74°C in a 1.5L stainless steel mix tank. The water seat is mixed with an IKA mixer (Model RW 20 DZM) at about 1000 rpm using an impeller with about 5.1 cm diameter blades. The mixture is also milled at the same time. About 21.8 g of DC CF-1469 silicone emulsion is added to the mix tank, with mixing. A mixture of about 86.7 g of the propane ester quat and 12 g of ethanol, pre-heated to about 82°C, is then slowly added to the water seat, injected at the impeller blades via a gravity-fed drop funnel. The mixer rpm is increased to about 1500 rpm during this addition. About 0.3 g of a CaCl_2 solution (25%) is added to reduce viscosity of the mixture and the mixer rpm is reduced to about 1000 rpm. About 0.2 g of a 1.5% Kathon solution is added. The mixture is chilled in an ice water bath while still mixing. The mill is turned off at this point. Another 0.3 g of the 25% CaCl_2 solution is added when the mixture temperature reaches about 27°C. The mixing is stopped when the batch temperature reaches about 24°C.

Example IX

The making procedure of Example IX is similar to that of Example VIII, except that about 12 g of an unemulsified 50 cSt PDMS is used instead of the 350 cSt PDMS emulsion.

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<u>EXAMPLES</u>		X	XI	XII
<u>Components</u>		<u>Wt. %</u>	<u>Wt. %</u>	<u>Wt. %</u>
	Ester Quat Compound (1)	11.6	11.6	11.6
	(Aminopropyl)methyl/di-			
5	methylsiloxane copolymer	0.7	-	-
	(Aminoethylaminopropyl)-			
	dimethylsiloxane copolymer	-	0.7	-
	Polyethyleneoxy/poly-			
	propyleneoxy/polydimethyl-			
10	siloxane copolymer	-	-	0.7
	HCl (3.65%)	1.1%	1.1%	0.5%
	NaCl (25%)	0.2%	0.2%	0.2%
	Kathon CG® (1.5%)	0.02%	0.02%	0.02%
	DC-2210® Antifoam (10%)	0.1%	0.1%	0.1%
15	Deionized Water	Balance	Balance	Balance

(1) Di(soft tallowoxyloxyethyl)dimethyl ammonium chloride of Example I.

20 Example X

About 11 g HCl solution and about 7 g of an unemulsified PDMS containing about 4 mole% of (3-aminopropyl)methyl siloxane comonomer are added with mixing to about 863 g deionized water pre-heated to about 68°C for about 2 minutes. This amino-functional silicone has a viscosity of from about 100 to about 200 cSt, and is available from Huls America, Piscataway, New Jersey. About 116 g of ester quaternary ammonium compound, pre-heated to about 66°C, is then slowly added to the water seat with high shear mixing. About half of the NaCl solution, followed by the antifoam, are added to the mixing vessel. The mixture is milled for about 10 minutes. The Kathon CG solution and the remainder of the NaCl solution are then added with mixing.

to that of Example X, except that about 7 g of an unemulsified PDMS containing about 4 mole % of N-(2-

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aminoethyl)-3-aminopropyl]methyl siloxane comonomer is used instead of the (3-aminopropyl)methyl/dimethylsiloxane copolymer. This amino-functional silicone has a viscosity of from about 50 to about 90 cSt, and is available from Huls America, Piscataway, New Jersey.

Example XII

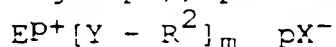
The making procedure of Composition XII is similar to that of Example X, except that about 7 g of Silwet® :-7001, a polyethyleneoxy/polypropyleneoxy/polydimethylsiloxane copolymer, is used. This alkoxyated silicone is available from Union Carbide Corporation, Danbury, Connecticut. This polyalkylenoxy PDMS derivative has a polydimethylsiloxane backbone, with some methyl groups replaced by $\text{C}_3\text{H}_6\text{-O-(C}_2\text{H}_4\text{O)}_a\text{-(C}_3\text{H}_6\text{O)}_b\text{-CH}_3$ groups wherein the $\text{C}_2\text{H}_4\text{O/C}_3\text{H}_6\text{O}$ ratio is about 40/60, with an average molecular weight of about 20,000, and a viscosity of about 1,400 cSt.

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What is claimed is:

1. A rinse-added fabric softening composition comprising
 (A) from about 5% to about 50%, preferably from about 6% to about 35%, more preferably from about 7% to about 32%, of a biodegradable cationic softener active containing at least one long hydrophobic group, with improved biodegradability as a result of the presence of ester linkages in the long hydrophobic groups,, preferably having the general formula:



wherein

p is 1 or 2;

m is 2 or 3;

each E is a nitrogenous quaternary group of charge p+;

each Y is -O-(O)C-, or -C(O)-O-;

each R² is a C₁₁-C₂₂ hydrocarbyl or substituted hydrocarbyl substituent; and

each X⁻ is any softener-compatible anion, preferably selected from the group consisting of: chloride; bromide; methyl sulfate; ethyl sulfate; formate; nitrate; and mixtures thereof, and, more preferably, wherein, in said formula, p is 1; m is 2; R² is a C₁₅-C₁₇ hydrocarbyl or substituted hydrocarbyl substituent;

(B) from about 0.2% to about 20% of silicone, preferably polydimethyl siloxane or derivative thereof, more preferably polydimethyl siloxane, having a viscosity of from about 2 to about 5000 cSt; and

(C) the balance aqueous liquid carrier optionally containing low molecular weight organic solvent that is highly soluble or miscible in water.

about 500 cSt, preferably from about 25 to about 200 cSt.

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3. The composition of Claim 1 or Claim 2 wherein the ratio of polydimethyl siloxane to said biodegradable cationic softener active is from about 2:100 to about 50:100, preferably from about 3:100 to about 35:100, more preferably from about 4:100 to about 25:100.
4. The composition of any of the above Claims wherein the low molecular weight organic solvent of (C) is selected from the group consisting of: (a) short chain alkyl alcohols; (b) alkylene glycols; (c) poly(alkylene glycols); (d) alkylene carbonates; and (e) mixtures thereof, preferably selected from the group consisting of ethanol, propanol, isopropanol, ethylene glycol, propylene glycol, propylene carbonate, diethylene glycol monobutyl ether, dipropylene glycol, 2-methyl-1,3 propanediol, and mixtures thereof.
5. The composition of any of the above Claims containing substituted polydimethyl siloxane selected from the group consisting of amino silicone; ethoxylated silicone; and mixtures thereof, preferably amino silicone.
6. The method of treating fabrics with the composition of any of the above Claims wherein the composition is added to provide at least 40 ppm of biodegradable cationic softener active (A) and at least 2 ppm of polydimethyl siloxane.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/02842A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D1/62 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 239 910 (PROCTER & GAMBLE ; PROCTER & GAMBLE EUROP (BE)) 7 October 1987 see page 11, paragraph 2 - page 12, line 24 see page 16, last paragraph - page 17, line 1; claims ---	1-6
X	US,A,4 789 491 (CHANG NIENYUAN J ET AL) 6 December 1988 see column 6, line 33 - column 8, line 2 see column 11, line 50 - column 12, line 26; claims ---	1-6
X	EP,A,0 370 675 (KAO CORP) 30 May 1990 see page 4, line 6 - line 31; claims --- -/--	1-6

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 95/02842

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 354 856 (COLGATE PALMOLIVE CO) 14 February 1990 see page 3, line 7 - line 37 see page 4, line 48 - page 5, line 22; claims ---	1-6
A	EP,A,0 255 711 (DOW CORNING) 10 February 1988 see the whole document ---	1-6
A	EP,A,0 459 822 (UNILEVER PLC ;UNILEVER NV (NL)) 4 December 1991 see the whole document ---	1-6
A	WO,A,92 01773 (PROCTER & GAMBLE) 6 February 1992 see claims ---	1-6
A	FR,A,2 318 268 (PROCTER & GAMBLE EUROP) 11 February 1977 see claims -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/02842

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP-A-0239910	07-10-87	GB-A-	2188653	07-10-87
		AU-B-	599966	02-08-90
		AU-A-	7096587	08-10-87
		CA-A-	1279448	29-01-91
		DE-A-	3782075	12-11-92
		IE-B-	60303	29-06-94
		JP-A-	63006168	12-01-88
		US-A-	4767547	30-08-88

US-A-4789491	06-12-88	EP-A-	0302567	08-02-89

EP-A-0370675	30-05-90	JP-A-	2139480	29-05-90
		JP-B-	4028826	15-05-92
		CA-A-	2003324	21-05-90
		DE-D-	68920006	26-01-95
		DE-T-	68920006	11-05-95
		ES-T-	2064460	01-02-95
		US-A-	5023003	11-06-91

EP-A-0354856	14-02-90	AU-B-	616990	14-11-91
		AU-A-	3941189	15-02-90
		GR-B-	1000488	30-07-92
		JP-A-	2154069	13-06-90
		TR-A-	24991	01-09-92
		US-A-	5051196	24-09-91

EP-A-0255711	10-02-88	US-A-	4767548	30-08-88
		CA-A-	1279156	22-01-91
		DE-A-	3773292	31-10-91
		JP-A-	63042978	24-02-88

EP-A-0459822	04-12-91	US-A-	5064544	12-11-91
		US-A-	5174911	29-12-92
		AU-B-	641014	09-09-93
		AU-A-	7737691	05-12-91
		CA-A-	2043503	02-12-91
		JP-A-	4257371	11-09-92

WO-A-9201773	06-02-92	AU-A-	8199791	18-02-92
		CA-A-	2087985	24-01-92

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat

Application No

PCT/US 95/02842

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9201773		CN-A- 1060125	08-04-92
		EP-A- 0540557	12-05-93
		NZ-A- 239069	27-06-94
		US-A- 5173201	22-12-92
<hr/>			
FR-A-2318268	11-02-77	GB-A- 1549180	01-08-79
		AT-B- 364431	27-10-81
		CA-A- 1102511	09-06-81
		CH-A- 614473	30-11-79
		DE-A- 2631419	03-02-77
		JP-A- 52053094	28-04-77
		NL-A- 7607870	18-01-77
		SE-B- 418512	09-06-81
		SE-A- 7608101	17-01-77
		CA-A- 1118965	02-03-82
		BE-A- 844200	17-01-77
		CA-A- 1085563	16-09-80
<hr/>			